Chapter 8

RELATED QUANTITIES

(a) Heat of Combustion and Potential Heat

by

Vytenis Babrauskas

THEORY

In a combustion reaction, the essential quantity is the heat of reaction. Since in typical combustion reactions we are dealing with constant-pressure, rather than constant-volume systems, it is most convenient to work with enthalpies, rather than energies. The enthalpy, H (kJ), is defined as:

$$H \equiv U + PV$$

where U is the energy (kJ), P is the pressure (kPa), and V is the volume (m^3). In thermodynamics and engineering calculations, specific enthalpy, h, is often used (and also specific energy, u). Molar units (kJ/mol) for these terms are typical in thermodynamics calculations, while in engineering computations it is often convenient to adopt mass (kJ/kg) units.

The enthalpy scale does not have an absolute zero. Instead, the actual values are always treated in reference to certain substances in certain states, which have an intrinsic 'enthalpy of formation' defined to be ≡ 0. Thus, solid at the standard reference temperature of 298 K, for example, carbon (graphite) and diatomic oxygen gas (O_2) are both defined to have an enthalpy of formation, $\Delta h_f \equiv 0$. Heat will be liberated if we combine carbon and oxygen,

$$C + O_2 \rightarrow CO_2$$

Heats of formation have to balance across a chemical equation. Since Δh_f for C and for O_2 are zero, the heat evolved from this reaction will, in fact, be the heat of formation of CO_2, which is -393.5 kJ/mol [1]. In general, we can write that the heat of reaction, $\Delta h°_r$, will be:

$$\Delta h_r^\circ = \sum_i^p n_i \Delta h_f^\circ - \sum_j^r n_j \Delta h_f^\circ$$

and with all of the enthalpy of formation terms, for both reactants 'r,' and products 'p,' being defined at the standard temperature of 298 K. Also, according to the above definition, it can be seen that the heat of reaction is negative for exothermic (heat-producing) reaction.

The (gross) heat of combustion is now defined as the heat of reaction for a combustion reaction, under the provisos:

- there is exactly 1 mole of fuel as the reactant
- that the fuel and the oxidant enter at 1 atmosphere pressure and 298 K temperature
- that, after an amount of heat equal to the heat of combustion is extracted, the products are also at 298 K and 1 atmosphere
- that the oxidant is gaseous oxygen
- that the primary products are liquid H_2O, gaseous CO_2, and gaseous N_2, and there is no CO or unburnt hydrocarbons. For combustibles containing atoms other than C, H, O, and N, other standard products are prescribed [2].

For convenience, in practical engineering use, the heat of combustion is usually redefined to be $-\Delta h_r$, and so as to be a *positive* number. In a few references, heats of combustion are tabulated as negative numbers—no different physics is implied there, merely an opposite sign convention.

When reactions take place under these conditions, the 'upper,' or 'gross' heat of combustion is realized. In a practical reaction, the products may not be the ideal products specified above; in such a case, the heat released will not be the gross heat of combustion.

The net heat of combustion

One special combustion condition is important enough that a new term is introduced for it. It turns out that many processes of interest in combustion end up with the products in such a state that the water in not liquefied, but remains a gas. In those cases, it is convenient to define a variant quantity, the 'lower,' or 'net,' heat of combustion. This is equal to the gross heat of combustion, minus the latent heat of water at 298 K. This is the quantity that is, in fact, much more commonly used in fire applications than is the gross heat of combustion. Since there is unique relationship between the amount of water produced in the combustion reaction and the amount of hydrogen in the fuel, the net heat of combustion can most simply be expressed as:

$$\Delta h^{l}_{c} = \Delta h^{u}_{c} - 0.219[\%H]$$

where Δh_c^u is the gross heat of combustion (MJ/kg), Δh_c^ℓ is the net heat of combustion (MJ/kg), and [%H] is the percent, by mass, of hydrogen in the fuel.

For common solid combustibles, the enthalpy of the reactant fuel is normally defined to have the fuel in its solid phase. Thus, to compute an energy balance in a room fire, it is *not* necessary to subtract the heat required to gasify the solid material, since this is already included in the definition for the heat of combustion. (In a practical computation, such as for a room fire, however, it may still be necessary to know the heat of gasification if *excess*, that is, unburnt, fuel is being pyrolyzed. The heat to gasify this excess fuel will then have to be taken into account as a heat loss term.)

Table 1, taken from Ref. [2] lists the heats of combustion of some common combustibles.

Measurement

1. *The gross heat of combustion*

The gross heat of combustion is normally measured in an oxygen bomb calorimeter. There are numerous variants in the design, construction and operation of such calorimeters. A typical unit, produced by Parr Instrument Co., Moline, Illinois (USA), is shown in Fig. 1. The monograph by Jessup [3] gives a good

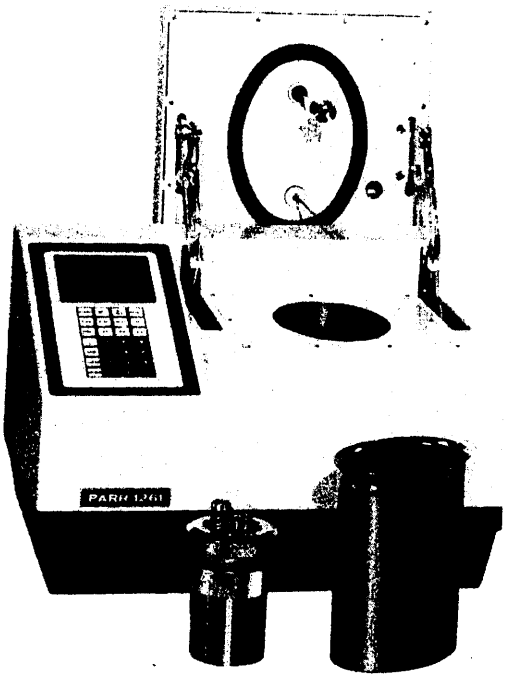

Figure 1. A typical oxygen bomb apparatus (Parr Instrument Co.).

Table 1A
Heats of Combustion and Related Properties for Pure, Simple Substances

Material	Composition	W Molecular Weight	Δh_c^u Gross (MJ/kg)	Δh_c^l Net (MJ/kg)	$\Delta h_c^l/r_o$ (MJ/kg O_2)	r_o Oxygen-fuel* Mass ratio	T_b Boiling temp. (°C)	Δh_v Latent Heat of Vaporization (kJ/kg)	C_{pl} Liquid Heat Capacity (kJ/kg-°C)	C_{pv} Vapor Heat Capacity (kJ/kg-°C)
acetaldehyde	C_2H_4O	44.05	27.07	25.07	13.81	1.816	20.8	—	1.94	1.24
acetic acid	$C_2H_4O_2$	60.05	14.56	13.09	12.28	1.066	118.1	395		1.11
acetone	C_3H_6O	58.08	30.83	28.56	12.96	2.204	56.5	501	2.12	1.29
acetylene	C_2H_2	26.04	49.91	48.22	15.70	3.072	−84.0	—	—	1.69
acrolein	C_3H_4O	56.06	29.08	27.51	13.77	1.998	52.5	505	—	1.17
acrylonitrile	C_3H_3N	53.06	33.16	31.92	14.11	2.262	77.3	615	2.10	1.20
(allene) → propadiene										
ammonium perchlorate†	NH_4ClO_4	117.49	2.35	2.16	3.97	0.545	—	—	—	
iso-amyl alcohol	$C_5H_{12}O$	88.15	37.48	34.49	12.67	2.723	132.0	501	2.90	1.50
aniline	C_6H_7N	93.12	36.44	34.79	13.06	2.663	184.4	478	2.08	1.16
benzaldehyde	C_7H_6O	106.12	33.25	32.01	13.27	2.412	179.2	385	1.61	
benzene	C_6H_6	78.11	41.83	40.14	13.06	3.073	80.1	389	1.72	1.05
benzoic acid†	$C_7H_6O_2$	122.12	26.43	25.35	12.90	1.965	250.8	415	—	0.85
benzyl alcohol	C_7H_8O	108.13	34.56	32.93	13.09	2.515	205.7	467	2.00	1.19
bicyclohexyl	$C_{12}H_{22}$	166.30	45.35	42.44	12.61	3.367	236.	263		
1,2-butadiene	C_4H_6	54.09	47.95	45.51	13.99	3.254	10.8	—	—	1.48
1,3-butadiene	C_4H_6	54.09	46.99	44.55	13.69	3.254	−4.4	—	—	1.47
(1,3-butadiyne) → diacetylene										
n-butane	C_4H_{10}	58.12	49.50	45.72	12.77	3.579	−0.5	—	2.30	1.68
iso-butane	C_4H_{10}	58.12	48.95	45.17	12.62	3.579	−11.8	—	—	1.67
1-butene	C_4H_8	56.10	48.44	45.31	13.24	3.422	−6.2	—	—	1.53
n-butylamine	$C_4H_{11}N$	73.14	41.75	38.45	12.84	2.994	77.8	372	2.57	1.62
d-camphor†	$C_{10}H_{16}O$	152.23	38.75	36.44	12.84	2.838	203.4	—	—	0.82
carbon†	C	12.01	32.80	32.80	12.31	2.664	4200.	—	—	0.71
carbon disulfide	CS_2	76.13	6.34	6.34	5.03	1.261	46.5	351	1.00	0.60
carbon monoxide	CO	28.01	10.10	10.10	17.69	0.571	−191.3	—	—	1.04
cellulose†	$C_6H_{10}O_5$	162.14	17.47	16.12	13.61	1.184	—	—	1.16	—
(chloroethylene) → vinyl chloride										
(chloroform) → trichloromethane										
chlorotrifluoroethylene	C_2F_3Cl	116.47	2.00	2.00	3.64	0.549	−28.3	188	1.34	0.72
m-cresol	C_7H_8O	108.13	34.26	32.64	12.98	2.515	202.2	399	2.00	1.13
cumene	C_9H_{12}	120.19	43.40	41.20	12.90	3.195	152.3	312	1.77	1.26
cyanogen	C_2N_2	52.04	21.06	21.06	17.12	1.230	−21.2	—	—	1.12
cyclobutane	C_4H_8	56.10	48.91	45.77	13.38	3.422	12.9	—	—	1.29

cyclohexane	C_6H_{12}	84.16	46.58	43.45	12.70	3.422	80.7	357	1.84	1.26
cyclohexene	C_6H_{10}	82.14	45.67	42.99	12.99	3.311	82.8	371	1.80	1.28
cyclohexylamine	$C_6H_{13}N$	99.18	41.05	38.17	12.79	2.984	134.5			
cyclopentane	C_5H_{10}	70.13	46.93	43.80	12.80	3.422	49.3	389	2.23	1.18
cyclopropane	C_3H_6	42.08	49.70	46.57	13.61	3.422	−32.9	—	1.92	1.33
(decahydronaphthalene) → *cis*-decalin										
cis-decalin	$C_{10}H_{18}$	138.24	45.49	42.63	12.70	3.356	195.8	309	1.67	1.21
n-decane	$C_{10}H_{22}$	142.28	47.64	44.24	12.69	3.486	174.1	276	2.19	1.65
diacetylene	C_4H_2	50.06	46.60	45.72	15.89	2.877	10.3	—	—	1.47
(diamine) → hydrazine										
diborane	H_6B_2	27.69	79.80	79.80	23.02	3.467	−92.5	—	—	1.75
dichloromethane	CH_2Cl_2	84.94	6.54	6.02	10.65	0.565	39.7	330	1.18	0.60
diethyl cyclohexane	$C_{10}H_{20}$	140.26	46.30	43.17	12.58	3.422	174.		1.87	
diethyl ether	$C_4H_{10}O$	74.12	36.75	33.79	13.04	2.590	34.6	360	2.34	1.52
(2,4 diisocyanotoluene) → toluene diisocyanate										
(diisopropyl ether) → *iso*-propyl ether										
dimethylamine	C_2H_7N	45.08	38.66	35.25	13.24	2.662	6.9	—	—	1.60
(dimethyl aniline) → xylidene										
dimethyldecalin	$C_{12}H_{22}$	166.30	45.70	42.79	13.15	3.254	220.	260		
(dimethyl ether) → methyl ether										
1,1-dimethylhydrazine (UDMH)	$C_2H_8N_2$	60.10	32.95	30.03	14.10	2.130	25.	578	2.73	
dimethyl sulfoxide	C_2H_6SO	78.13	29.88	28.19	15.30	1.843	189.	677	1.89	1.14
1,3 dioxane	$C_4H_8O_2$	88.10	26.57	24.58	9.66	2.543	105.	404		
1,4 dioxane	$C_4H_8O_2$	88.10	26.83	24.84	9.77	2.543	101.1	406	1.74	1.07
ethane	C_2H_6	30.07	51.87	47.49	12.75	3.725	−88.6	—	—	1.75
ethanol	C_2H_6O	46.07	29.67	26.81	12.87	2.084	78.5	837	2.43	1.42
(ethene) → ethylene										
ethyl acetate	$C_4H_8O_2$	88.10	25.41	23.41	12.89	1.816	77.2	367	1.94	1.29
ethyl acrylate	$C_5H_8O_2$	100.12	27.44	25.69	13.39	1.918	100.	290		1.14
ethylamine	C_2H_7N	45.08	38.63	35.22	13.23	2.662	16.5	—	2.89	1.61
ethyl benzene	C_8H_{10}	106.16	43.00	40.93	12.93	3.165	136.1	339	1.75	1.21
ethylene	C_2H_4	28.05	50.30	47.17	13.78	3.422	−103.9	—	2.38	1.56
ethylene glycol	$C_2H_6O_2$	62.07	19.17	17.05	13.22	1.289	197.5	800	2.43	1.56
ethyler.e oxide	C_2H_4O	44.05	29.65	27.65	15.23	1.816	10.7	—	1.97	1.10
(ethylene trichloride) → trichloroethylene										
(ethyl ether) → diethyl ether										
formaldehyde	CH_2O	30.03	18.76	17.30	16.23	1.066	−19.3	—	—	1.18
formic acid	CH_2O_2	46.03	5.53	4.58	13.15	0.348	100.5	476	2.15	0.98
furan	C_4H_4O	68.07	30.61	29.32	13.86	2.115	31.4	398	1.69	0.96
α-D-glucose†	$C_6H_{12}O_6$	180.16	15.55	14.08	13.21	1.066	—	—	—	—

Table 1A—*contd.*

Material	Composition	W Molecular Weight	Δh_c^u Gross (MJ/kg)	Δh_c^l Net (MJ/kg)	$\Delta h_c^l/r_o$ (MJ/kg 0_2)	r_o Oxygen-fuel Mass ratio	T_b Boiling temp. (°C)	Δh_v Latent Heat of Vaporization (kJ/kg)	C_{pl} Liquid Heat Capacity (kJ/kg-°C)	C_{pv} Vapor Heat Capacity (kJ/kg-°C)
(glycerine) → glycerol										
glycerol	$C_3H_8O_3$	92.10	17.95	16.04	13.19	1.216	290.0	800	2.42	1.25
(glycerol trinitrate) → nitroglycerin										
n-heptane	C_7H_{16}	100.20	48.07	44.56	12.68	3.513	98.4	316	2.20	1.66
n-heptene	C_7H_{14}	98.18	47.44	44.31	12.95	3.422	93.6	317	2.17	1.58
hexadecane	$C_{16}H_{34}$	226.43	47.25	43.95	12.70	3.462	286.7	226	2.22	1.64
hexamethyldisiloxane	$C_6H_{18}Si_2O$	162.38	38.30	35.80	15.16	2.364	100.1	192	2.01	—
(hexamethylenetetramine) → methenamine										
n-hexane	C_6H_{14}	86.17	48.31	44.74	12.68	3.528	68.7	335	2.24	1.66
n-hexene	C_6H_{12}	84.16	47.57	44.44	12.99	3.422	63.5	333	2.18	1.57
hydrazine	H_4N_2	32.05	52.08	49.34	49.40	0.998	113.5	1180	3.08	1.65
hydrazoic acid	HN_3	43.02	15.28	14.77	79.40	0.186	35.7	690	—	1.02
hydrogen	H_2	2.00	141.79	130.80	16.35	8.000	−252.7	—	—	14.42
(hydrogen azide) → hydrazoic acid										
hydrogen cyanide	HCN	27.03	13.86	13.05	8.82	1.480	25.7	933	2.61	1.33
hydrogen sulfide	H_2S	34.08	48.54	47.25	16.77	2.817	−60.3	548	—	1.00
maleic anhydride†	$C_4H_2O_3$	74.04	18.77	18.17	14.01	1.297	202.0	—	—	—
melamine†	$C_3H_6N_6$	126.13	15.58	14.54	12.73	1.142	—	—	—	—
methane	CH_4	16.04	55.50	50.03	12.51	4.000	−161.5	—	—	2.23
methanol	CH_4O	32.04	22.68	19.94	13.29	1.500	64.8	1101	2.37	1.37
methenamine†	$C_6H_{12}N_4$	140.19	29.97	28.08	13.67	2.054	—	—	—	—
2-methoxyethanol	$C_3H_8O_2$	76.09	24.23	21.92	13.03	1.682	124.4	583	2.23	—
methylamine	CH_5N	31.06	34.16	30.62	13.21	2.318	−6.3	—	—	1.61
(2-methyl 1-butanol) → *iso*-amyl alcohol										
(methyl chloride) → dichloromethane										
methyl ether	C_2H_6O	46.07	31.70	28.84	13.84	2.084	−24.9	—	—	1.43
methyl ethyl ketone	C_4H_8O	72.10	33.90	31.46	12.89	2.441	79.6	434	2.30	1.43
1-methylnaphthalene	$C_{11}H_{10}$	142.19	40.88	39.33	12.95	3.038	244.7	323	1.58	1.12
methyl methacrylate	$C_5H_8O_2$	100.11	27.37	25.61	12.33	2.078	101.0	360	1.91	—
methyl nitrate	CH_3NO_3	77.04	8.67	7.81	75.10	0.104	64.6	409	2.04	0.99
(2-methyl propane) → *iso*-butane										
naphthalene†	$C_{10}H_8$	128.16	40.21	38.84	12.96	2.996	217.9	—	1.18	1.03
nitrobenzene	$C_6H_5NO_2$	123.11	25.11	24.22	14.90	1.625	210.7	330	1.52	—
nitroglycerin	$C_3H_5N_3O_9$	227.09	6.82	6.34	—	—	unstable	462	1.49	—
nitromethane	CH_3NO_2	61.04	11.62	10.54	15.08	0.699	101.1	567	1.74	0.94
n-nonane	C_9H_{20}	128.25	47.76	44.33	12.69	3.493	150.6	295	2.10	1.65

cyclotetrasiloxane	$C_8H_{24}Si_4O_4$	296.62	26.90	25.10	14.56	1.725	175.0	127	1.68	—
n-octane	C_8H_{18}	114.22	47.90	44.44	12.69	3.502	125.6	301	2.20	1.65
iso-octane	C_8H_{18}	114.22	47.77	44.31	12.65	3.502	117.7	272	2.15	1.65
1-octene	C_8H_{10}	112.21	47.33	44.20	12.92	3.422	121.3	301	2.19	1.59
(1-octylene) → 1-octene										
1,2-pentadiene	C_5H_8	68.11	47.31	44.71	13.60	3.288	44.9	405	2.21	1.55
n-pentane	C_5H_{12}	72.15	48.64	44.98	12.68	3.548	36.0	357	2.33	1.67
1-pentene	C_5H_{10}	70.13	47.77	44.64	13.04	3.422	30.0	359	2.16	1.56
phenol†	C_6H_6O	94.11	32.45	31.05	13.05	2.380	181.8	433	1.43	1.10
phosgene	$COCl_2$	98.92	1.74	1.74	10.74	0.162	8.3	247	1.02	0.58
propadiene	C_3H_4	40.06	48.54	46.35	14.51	3.195	−34.6	—	—	1.44
propane	C_3H_8	44.09	50.35	46.36	12.78	3.629	−42.2	—	2.23	1.67
n-propanol	C_3H_8O	60.09	33.61	30.68	12.81	2.396	97.2	686	2.50	1.45
iso-propanol	C_3H_8O	60.09	33.38	30.45	12.71	2.396	80.3	663	2.42	1.48
propene	C_3H_6	42.08	48.92	45.79	13.38	3.422	−47.7	—	—	1.52
(*iso*-propylbenzene) → cumene										
(propylene) → propene										
iso-propyl ether	$C_6H_{14}O$	102.17	39.26	36.25	12.86	2.819	67.8	286	2.14	1.55
propyne	C_3H_4	40.06	48.36	46.17	14.45	3.195	−23.3	—	—	1.51
styrene	C_8H_8	104.14	- 2.21	40.52	13.19	3.073	145.2	356	1.76	1.17
sucrose†	$C_{12}H_{22}O_{11}$	342.30	16.49	15.08	13.44	1.122	—	—	1.24	—
(1,2,3,4-tetrahydronaphthalene) → tetralin										
tetralin	$C_{10}H_{12}$	132.20	42.60	40.60	12.90	3.147	207.0	425	1.64	1.19
tetranitromethane	CN_4O_8	196.04	2.20	2.20	—	—	125.7	196—	—	
toluene	C_7H_8	92.13	42.43	40.52	12.97	3.126	110.4	360	1.67	1.12
toluene diisocyanate	$C_9H_6N_2O_2$	174.16	24.32	23.56	13.50	1.746	120.0	—	1.65	—·
triethanolamine	$C_6H_{15}NO_3$	149.19	29.29	27.08	15.30	1.770	360.0	—	—	—
triethylamine	$C_6H_{15}N$	101.19	43.19	39.93	12.95	3.083	89.5	303	2.22	1.59
1,1,2-trichloroethane	$C_2H_3Cl_3$	133.42	7.77	7.28	11.02	0.660	114.0	260	1.11	0.67
trichloroethylene	C_2HCl_3	131.40	6.77	6.60	12.05	0.548	86.9	245	1.07	0.61
trichloromethane	$CHCl_3$	119.39	3.39	3.21	9.60	0.335	61.7	249	0.97	0.55
trinitromethane	CHN_3O_6	151.04	3.41	3.25	—	—	unstable	—	—	—
trinitrotoluene†	$C_7H_5N_3O_6$	227.13	15.12	14.64	19.80	0.740	240.0	322	1.40	—
trioxane	$C_3H_6O_3$	90.08	16.57	15.11	14.17	1.066	114.5	450	—	—
urea†	CH_4ON_2	60.06	10.52	9.06	11.34	0.799	—	—	—	1.55
vinyl acetate	$C_4H_6O_2$	86.09	24.18	22.65	13.54	1.673	72.5	167	2.00	1.05
vinyl acetylene	C_4H_4	52.07	47.05	45.36	14.76	3.073	5.1	—	—	1.41
vinyl bromide	C_2H_3Br	106.96	12.10	11.48	13.95	0.823	15.6	—	2.42	0.53
vinyl chloride	C_2H_3Cl	62.50	20.02	16.86	11.97	1.408	−13.8	—	—	0.86
(vinyl trichloride) → 1,1,2-trichloroIthane										
xylenes	C_8H_{10}	106.16	42.89	40.82	12.90	3.165	138–144	343	1.72	1.21
xylidene	$C_8H_{11}N$	121.22	38.28	36.29	12.79	2.838	192.7	366	1.77	—

† Denotes substance in crystalline solid form; otherwise, liquid if $T_b > 25°C$, gaseous if $T_b < 25°C$.

Table 1B
Heats of Combustion and Related Properties for Plastics

Material	Unit Composition	W Molecular Weight	Δh_c^u Gross (MJ/kg)	Δh_c^l Net (MJ/kg)	$\Delta h_c^l/r_o$ (MJ/kg O_2)	r_o Oxygen-fuel Mass ratio	C_{ps} Heat Capacity Solid (kJ/kg-°C)
acrylonitrile-butadiene styrene copolymer	—	—	35.25	33.75			1.41–1.59
bisphenol A epoxy	$C_{11.85}H_{20.37}O_{2.83}N_{0.3}$	212.10	33.53	31.42	13.41	2.343	
butadiene-acrylonitrile 37% copolymer	—	—	39.94				
butadiene/styrene 8.58% copolymer	$C_{4.18}H_{6.09}$	56.30	44.84	42.49	13.11	3.241	1.94
butadiene/styrene 25.5% copolymer	$C_{4.60}H_{6.29}$	61.55	44.19	41.95	13.07	3.209	1.82
cellulose acetate (triacetate)	$C_{12}H_{16}O_8$	288.14	18.88	17.66	13.25	1.333	1.34
cellulose acetate-butyrate	$C_{12}H_{18}O_7$	274.27	23.70	22.3	14.67	1.517	1.70
epoxy, unhardened	$C_{31}H_{36}O_{5.5}$	496.63	32.92	31.32	13.05	2.400	
epoxy, hardened	$C_{39}H_{40}O_{8.5}$	644.74	30.27	28.90	13.01	2.221	
melamine formaldehyde (Formica)	$C_6H_6N_6$	162.08	19.33	18.52	12.51	1.481	1.46
nylon 6	$C_6H_{11}NO$	113.08	30.1 –31.7	28.0 –29.6	12.30	2.335	1.52
nylon 6,6	$C_{12}H_{22}N_2O_2$	226.16	31.6 –31.7	29.5 –29.6	12.30	2.405	1.70
nylon 11 (Rilsan)	$C_{11}H_{21}NO$	183.14	36.99	34.47	12.33	2.796	1.70–2.30
phenol formaldehyde -foam	$C_{15}H_{12}O_2$	224.17	27.9 –31.6 21.6 –27.4	26.7 –30.4 20.2 –26.2	11.80	2.427	1.70
polyacenaphthalene	$C_{12}H_8$	152.14	39.23	38.14	12.95	2.945	
polyacrylonitrile	C_3H_3N	53.04	32.22	30.98	13.70	2.262	1.50
polyallylphthalate (polyamides) → nylon	$C_{14}H_{14}O$	198.17	27.74	26.19	9.54	2.745	
poly-1,4-butadiene	C_4H_6	54.05	45.19	42.75	13.13	3.256	
poly-1-butene	C_4H_8	56.05	46.48	43.35	12.65	3.426	1.88
polycarbonate	$C_{16}H_{14}O_3$	254.19	30.99	29.78	13.14	2.266	1.26
polycarbon suboxide	C_3O_2	68.03	13.78	13.78	14.64	0.941	
polychlorotrifluorethylene	C_2F_3Cl	116.47	1.12	1.12	2.04	0.549	0.92
polydiphenylbutadiene	$C_{16}H_{10}$	202.18	39.30	38.2	13.05	2.928	
polyester, unsaturated	$C_{5.77}H_{6.25}O_{1.63}$	101.60	21.6 –29.8	20.3 –28.5	11.90	2.053	1.20–2.30

polyether, chlorinated	$C_8H_8OCl_2$	194.97	[illegible]	[illegible]	[illegible]	[illegible]	
polyethylene	C_2H_4	28.03	46.2 –46.5	43.1 –43.4	12.63	3.425	1.83–2.30
polyethylene oxide	C_2H_4O	44.02	26.65	24.66	13.57	1.817	
polyethylene terephthalate	$C_{10}H_8O_4$	192.11	22.18	21.27	12.77	1.666	1.00
polyformaldehyde	CH_2O	30.01	16.93	15.86	14.88	1.066	1.46
poly-1-hexene sulfone	$C_6H_{12}SO_2$	148.13	29.78	28.00	14.40	1.944	
polyhydrocyanic acid	HCN	27.02	23.26	22.45	15.17	1.480	
(polyisobutylene) → poly-1-butene							
polyisocyanurate foam	—		26.3	22.2 –26.2			
polyisoprene	C_5H_8	68.06	44.90	42.30	12.90	3.291	
poly-3-methyl-1-butene	C_5H_{10}	70.06	46.55	43.42	12.67	3.426	
polymethyl methacrylate	$C_5H_8O_2$	100.06	26.64	24.88	12.97	1.919	1.44
poly-4-methyl-1-pentene	C_6H_{12}	84.08	46.52	43.39	12.67	3.425	2.18
poly-α-methylstyrene	C_9H_{10}	118.11	42.31	40.45	13.00	3.116	
polynitroethylene	$C_2H_3O_2N$	73.03	15.96	15.06	19.64	0.767	
polyoxymethylene	CH_2O	30.01	16.93	15.65	14.68	1.066	
polyoxytrimethylene	C_3H_6O	58.04	31.52	29.25	13.27	2.205	
poly-1-pentene	C_5H_{10}	70.06	45.58	42.45	12.39	3.426	
polyphenylacetylene	C_8H_6	102.09	40.00	38.70	13.00	2.978	
polyphenylene oxide	C_6H_6O	120.09	34.59	33.13	13.09	2.531	1.34
polypropene sulfone	$C_3H_6SO_2$	106.10	23.82	22.58	16.64	1.357	
poly-β-propiolactone	$C_3H_4O_2$	72.14	19.35	18.13	13.62	1.331	
polypropylene	C_3H_6	42.04	46.37	43.23	12.62	3.824	2.10
polypropylene oxide	C_3H_6O	58.04	31.17	28.90	13.11	2.205	
polystyrene	C_8H_8	104.10	41.4 –42.5	39.7 –39.8	12.93	3.074	1.40
polystyrene-foam	—		39.7	35.6 –40.8			
polystyrene-foam, FR	—		41.2 –42.9				
polysulfones, butene	$C_4H_8SO_2$	120.11	24.04–26.47	22.25–25.01	14.79	1.598	1.30
polysulfur	S	32.06	9.72	9.72	9.74	0.998	
polytetrafluoroethylene	C_2F_4	100.02	5.00	5.00	7.81	0.640	1.02
polytetrahydrofuran	C_4H_8O	72.05	34.39	31.85	13.04	2.443	
polyurea	$C_{15}H_{18}O_4N_4$	318.20	24.91	23.67	13.45	1.760	
polyurethane	$C_{6.3}H_{7.1}NO_{2.1}$	130.30	23.90	22.70	13.16	1.725	1.75–1.84
polyurethane-foam	—		26.1 –31.6	23.2 –28.0			
polyurethane-foram, FR	—		24.0 –25.0				
polyvinyl acetate	$C_4H_6O_2$	86.05	23.04	21.51	12.86	1.673	
polyvinyl alcohol	C_2H_4O	44.03	25.00	23.01	12.66	1.817	1.70
polyvinyl butyral	$C_8H_{14}O_2$	142.10	32.90	30.70	13.00	2.365	
polyvinyl chloride	C_2H_3Cl	62.48	17.95	16.90	12.00	1.408	0.90–1.20
polyvinyl-foam	—		22.83				1.30–2.10
polyvinyl fluoride	C_2H_3F	46.02	21.70	20.27	10.60	1.912	
polyvinylidene chloride	$C_2H_2Cl_2$	96.93	10.52	10.07	12.21	0.825	1.34
polyvinylidene fluoride	$C_2H_2F_2$	64.02	14.77	14.08	11.26	1.250	1.38
urea formaldehyde	$C_3H_6O_2N_2$	102.05	15.90	14.61	13.31	1.098	1.60–2.10
urea formaldehyde-foam	—	—	14.80				

Table 1C
Heat of Combustion of Miscellaneous Substances

Material	Δh_c^u Gross (MJ/kg)	Δh_c^f Net (MJ/kg)
acetate (see cellulose acetate)		
acrylic fiber	30.6–30.8	
blasting powder	2.1–2.4	
butter	38.5	
celluloid (cellulose nitrate and camphor)	17.5–20.6	16.4–19.2
cellulose acetate fiber, $C_6H_{12}O_6$	17.8–18.4	16.4–17.0
cellulose diacetate fiber, $C_{10}H_{14}O_7$	18.7	
cellulose nitrate, $C_6H_9N_1O_7/C_6H_8N_2O_9/C_6H_7N_3O_{11}$	9.11–13.48	
cellulose triacetate fiber, $C_{12}H_{16}O_8$	18.8	17.6
charcoal	33.7–34.7	33.2–34.2
coal-anthracite	30.9–34.6	30.5–34.2
-bituminous	24.7–36.3	23.6–35.2
coke	28.0–31.0	28.0–31.0
cork	26.1	
cotton	16.5–20.4	
dynamite	5.4	
epoxy, $C_{11.9}H_{20.4}O_{2.8}N_{0.3}/C_{6.064}H_{7.550}O_{1.222}$	32.8–33.5	31.1–31.4
fat, animal	39.8	
flint powder	3.0–3.1	
fuel oil-No. 1	46.1	
-No. 6	42.5	
gasketing-chlorosulfonated polyethylene (Hypalon)	28.5	
-vinylidene fluoride/hexafluoropropylene (Fluorel, Viton A)		
gasoline	14.0–15.1	
jet fuel-JP1	46.8	43.7
-JP3		43.0
-JP4		43.5
-JP5	46.6	43.5
kerosene (jet fuel A)	45.9	43.0
lanolin (wool fat)	46.4	43.3
lard	40.8	
leather	40.1	
lignin, $C_{2.6}H_3O$	18.2–19.8	
lignite	24.7–26.4	23.4–25.1
	22.4–33.3	

modacrylic fiber	24.7	
naphtha	43.0–47.1	40.9–43.9
neoprene, $C_5H_5C\ell$-gum	24.3	
-foam	9.7–26.8	
Nomex (polymethaphenylene isophthalamide) fiber, $C_{14}H_{10}O_2N_2$	27.0–28.7	
oil-castor	37.1	
-linseed	39.2–39.4	
-mineral	45.8–46.0	
-olive	39.6	
-solar	41.8	
paper-brown	16.3–17.9	
-magazine	12.7	
-newsprint	19.7	
-wax	21.5	
paraffin wax	46.2	43.1
peat	16.7–21.6	
petroleum jelly ($C_{7.118}H_{12.957}O_{0.091}$)	45.9	
rayon fiber	13.6–19.5	
rubber-buna N	34.7–35.6	
-butyl	45.8	
-isoprene (natural) C_5H_8	44.9	42.3
-latex foam	33.9–40.6	
-GRS	44.2	
-tire, auto	32.6	
silicone rubber (SiC_2H_6O)	15.5–16.8	
-foam	14.0–19.5	
sisal	15.9	
spandex fiber	31.4	
starch	17.6	16.2
straw	15.6	
sulfur-rhombic		9.28
-monoclinic		9.29
tobacco	15.8	
wheat	15.0	
wood-beech	20.0	18.7
-birch	20.0	18.7
-douglas fir	21.0	19.6
-maple	19.1	17.8
-red oak	20.2	18.7
-spruce	21.8	20.4
-white pine	19.2	17.8
-hardboard	19.9	
woodflour	19.8	
wool	20.7–26.6	

Table 1D
Heats of Combustion for Metals

Material	Δh_c (MJ/kg)
Pure elements	
aluminum	31.04
beryllium	66.43
copper	2.45
iron	7.39
magnesium	24.72
manganese	7.01
molybdenum	6.13
nickel	4.10
tantalum	5.66
tin	3.73
titanium	19.71
zinc	5.37
zirconium	12.07
Copper alloys	
bronze (88 Cu/10 Sb/2 Zn)	2.64
red brass (85 Cu/15 Zn)	2.89
cartridge brass (70 Cu/30 Zn)	3.33
yellow brass (60 Cu/40 Zn)	3.62
Iron alloys	
carbon steels	7.4–7.5
stainless steels	7.7–8.4
Nickel alloys	
Inconel 600	5.40
Monel 400	3.60

discussion of the procedures and calculations in detail. Here, we will merely describe the basic procedure qualitatively.

The method involves burning of a small sample in a compressed oxygen atmosphere within a closed vessel which retains all the products of combustion. The bomb is typically made from stainless steel, and may have an inside volume of several hundred mL. Solid specimens are normally ground up to a fine powder, then pressed into pellet form. Liquid samples are used without special preparation. The quantity of specimen is typically in the vicinity of 1 g. Once a prepared specimen is placed inside the bomb, provisions for its ignition are made by installing a length of thin platinum or Chromel (nickel-alloy) wire inside, touching the specimen. Normally, 1 mL of water is also added to the bomb. The bomb is then closed and filled with oxygen, typically to about 30 atmospheres. Next, the bomb is set in a water bath (which contains an accurately weighed amount of water), the top is covered, and a precision thermometer (readable to 0.002 °C for normal work, and to 0.0003 °C for high-precision experiments) is inserted into the water bath. The water bath is surrounded by an insulating jacket, to minimize heat exchange with the room. A stirrer is also located in the water bath. This stirrer is run for several minutes, and the water jacket temperature is monitored or plotted. Then, an electric current is passed through the wire to

achieve ignition. The wire is partly consumed during this firing. The temperature of the water bath continues to be plotted. The temperature rises to a value only a few °C above the original temperature, then very slowly decays due to convective losses into the room. The heat released during the combustion is, roughly speaking, represented as this rise in the water bath temperature.

Corrections are made to account for the convective heat exchange with the room, both before and after the combustion. Corrections are also made for any benzoic acid added (which may have been needed as a combustion promoter) and for the amount of ignition wire which was consumed. When testing specimens containing elements other than C, H, and O, it is usually necessary to wash out the bomb and chemically analyze the residues, and then to make appropriate corrections. For example, specimens containing sulfur will tend to produce sulfuric acid, H_2SO_4, in the bomb, rather than the standard product, gaseous SO_2. Some nitric acid also tends to be produced from nitrogenated species, instead of simply yielding the assumed N_2 gas. Thus, a nitric acid correction is necessary. In general, any time products other than CO_2, H_2O, N_2, and SO_2 are found or can be expected, special analysis procedures are necessary. The treatises by Rossini [4] and Skinner [5] give the requisite background and details for many such calculations, including the combustion of metals.

In the cases of materials with low heats of combustion, some potentially combustible specimen residue may sometimes be found unburned, once the bomb is opened. In such cases, the test is repeated with a combustion promoter (typically powdered benzoic acid, chosen because of its well-known heat of combustion) being added in with the specimen. Conversely, for specimens which are so fast-burning as to potentially cause damage to some of the fittings inside the bomb, some water is typically added. Highly volatile samples, whose exact weight would otherwise be difficult to control, are often sealed inside a glass ampoule. The ampoule is placed in the bomb, with the ignition wire placed around it. The thermal expansion causes the ampoule to break, with its contents being released and burned.

Special purpose bombs include ones which can withstand higher pressures, used for testing of explosives, and ones made of special materials, intended to withstand the attack of certain corrosive agents.

For the results to be accurate, the bomb has to be calibrated by using a standard reference material, most typically benzoic acid. When properly calibrated, some bomb calorimeters can produce results with a precision of 0.05% [3].

The actual operating procedures that are followed should be based on both the manufacturer's instructions, and the relevant standard test method being used. In the United States, the primary methods published by ASTM are D 3286 [6] and D 2015 [7]. The former describes tests with what used to be called the

'isothermal jacket' calorimeter, recently renamed as the 'isoperibol jacket' calorimeter, i.e., one where the outer jacket is well-enough insulating so as to be at nearly the room temperature; while the latter provides for the 'adiabatic jacket' calorimeter, one where the temperature of the jacket is progressively raised to track closely the water bath temperature.

The experimental procedures described here can only treat homogenous specimens. If the test article is non-homogenous or composite, to determine its gross heat of combustion usually requires that the layers be separated, that their relative weight fractions be determined, and then that a homogenous specimen by tested from each layer separately. In some isolated cases it may be possible to prepare a test pellet which adequately represents the mass fractions of the product to be tested, but this should not, in the general case, be presumed.

2. *The net heat of combustion*

In view of its greater utility, it is unfortunate that there are no direct experimental methods available for measuring the net heat of combustion. When net heat of combustion values are required, the gross heat of combustion is first determined, as described above, then the net heat of combustion is computed, as shown in the previous section, by determining the fraction of hydrogen in the sample material. This generally requires a separate analysis by an analytical laboratory.

3. *Potential heat*

The combustion conditions in the oxygen bomb (oxygen pressures of 30 atmospheres, no diluting nitrogen, and the concomitant high reaction temperatures) are very different from the conditions in building fires. In a typical building fire, the oxygen pressure will be 0.21 atmospheres maximum, nitrogen or the products of earlier combustion reactions will be present as diluents, and temperatures will rarely reach over 1200 °C. Thus, there are many materials which will not combust in building fire, for example, aluminum, which will burn in an oxygen bomb. Thus, when it comes to evaluating certain classes of materials, the heats of combustion reported from an oxygen bomb calorimeter test may not at all correspond to the enthalpy which may be contributed to a building fire. These classes of materials include many metals, and also products which are primarily inorganic, but which contain a small organic fraction as a binder, filler, etc.

To provide a better method of estimating the heat contributable from a fire than is obtained from simply using the oxygen bomb values, Loftus, Gross, and Robertson developed in 1961 a procedure which they termed the potential heat test [8]. This method uses an electric muffle furnace to expose a rectangular specimen, 12 mm by 19 mm by 76 mm in size, to a constant temperature of 750 °C for two hours. The (gross) heat of combustion represented by the specimen is determined before and after this thermal exposure. If a specimen is completely

consumed during the 750 °C exposure, then the potential heat is identical to the gross heat of combustion. If a residue remains, however, then the potential heat that is reported is equal to the original sample's heat of combustion, minus the heat of combustion of the residue.

This method came into some use during the late 1960s and early 1970s. For example, some requirements based on it were used in the 'Operation Breakthrough' housing program promoted by the U.S. Dept. of Housing and Urban Development in the early 1970s. The method has been published by the National Fire Protection Association as NFPA 259 [9], first being issued in 1976. Roundrobin data have also been reported [10].

The potential heat method did not achieve wider adoption, since, at the time that it was becoming known, true rate of heat release methods were first becoming available for use. In the potential heat test, the exposure to the specimen which represents the fire conditions is fixed at a constant-temperature condition of 750 °C for two hours. This is not an unreasonable representation for a post-flashover fire. However, this exposure condition cannot be varied to suit desired application conditions, cannot be expressed in terms of a surface heating flux (the representation needed for room fire modeling), and is not entirely appropriate for composite specimens which should be exposed only from their front surface. Thus, it can be considered largely superseded for most current applications. The one exception might be where fuel-load surveys are conducted for buildings or other occupancies. In those applications, detailed measurements of rate of heat release are usually precluded; tabulated values of potential heats, rather than oxygen bomb value heats of combustion might be more appropriate. Even here, however, tabulations of effective heats of combustion (see below) are coming to be available and would be preferred, where available.

4. *The effective heat of combustion.*

It is, at this point, important to distinguish between the theoretical heat of combustion, as defined above, and what might be termed the 'effective heat of combustion.' The concern of heat release rate measurements is to determine the heat being released in a fire environment. If a measure of the mass loss is available at the same time, it is possible to divide the heat obtained by the mass lost and obtain a quantity which is in units of MJ/kg. This will be termed the effective heat of combustion. It will always be lower than the theoretical net heat of combustion. For these two quantities to be equal (besides making sure that all reactants and products are at exactly 298 K, etc.) there would have to be:

— no CO, unburnt hydrocarbons, or similar products of incomplete combustion, and
— no fuel remaining unreacted, and no fuel unmixed with and, therefore, unable to fully react with the oxygen.

By contrast, the gross (or net) heat of combustion is not measured by introducing some measuring device into a fire. Since it is required that the reaction be complete, this must obviously be done under specialized conditions. These specialized conditions are created in a combustion bomb.

The potential heat, discussed in previous section, even though it is measured in a specialized apparatus, can, thus, be seen to be merely the effective heat of combustion for the rather artificial sample configuration and exposure conditions prescribed.

More typically, the effective heat of combustion is measured in either full-scale or bench-scale tests where the mass loss rate and the heat release rate are simultaneously measured with time-resolved instruments. (The effective heat of combustion could also be determined in cases where only the total heat liberated and the total specimen mass lost are known, but with the current availability of time-resolved instrumentation, one is usually not restricted to such overall measures.)

Finally, it should be emphasized that the effective heat of combustion is naturally obtained as a time-varying quantity during the combustion process. This information can often be used to deduce chemical changes, such as charring, occurring as the combustion progresses.

REFERENCES

1. Stull, D.R., and Prophet, H., JANAF Thermochemical Tables, Second Edition (NSRDS--NBS 37). [U.S.] Natl. Bur. Stand. (1971).
2. *Fire Protection Handbook*, 16th edition, pp. 5-117 to 5-125, A.E. Cote and J.L. Linville, eds., National Fire Protection Assn., Quincy, MA (1986).
3. Jessup, R.S., Precise Measurement of Heat of Combustion With a Bomb Calorimeter (NBS Monograph 7). [U.S.] Natl. Bur. Stand. (1959).
4. Rossini, F.D., ed., *Experimental Thermochemistry*, Vol. 1. Interscience Publishers, New York (1955).
5. Skinner, H.A., ed., *Experimental Thermochemistry*, Vol. 2. Interscience Publishers, New York (1962).
6. Standard Test Method for Gross Calorific Value of Coal and Coke by the Isoperibol-Jacket Bomb Calorimeter (D 3286). American Society for Testing and Materials, Philadelphia.
7. Standard Test Method for Gross Calorific Value of Coal and Coke by the Adiabatic Bomb Calorimeter (D 2015). American Society for Testing and Materials, Philadelphia.
8. Loftus, J.J., Gross, D., and Robertson, A.F., Potential Heat--A Method for Measuring the Heat Release of Materials in Building Fires, *ASTM Proc. 61*, 1336-48 (1961).

9. Standard Test Method for Potential Heat of Building Materials (NFPA 259). National Fire Protection Assn., Quincy, MA.
10. Gross, D., Interlaboratory Comparison of the Potential Heat Test Method, pp. 127-152 in *Fire Test Performance* (ASTM STP 464). American Society for Testing and Materials, Philadelphia (1970).